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PERFORMANCE OF SULFATION AND NITRATION PLATES USED TO MONITOR ATMOSPHERIC POLLUTANT DEPOSITION IN A REAL ENVIRONMENT

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ABSTRACT

Sulfation and nitration plates were exposed outdoors for various periods of time to evaluate their performance in a real environment. These passive monitors are used to estimate the deposition of pollutants on metallic surfaces, and thus to evaluate the influence of the atmosphere on the corrosion. Single-column ion chromatography was used to determine the quantity of anions absorbed on the plates. This technique is better than other analytical procedures such as turbidimetry or colorimetry because passive monitors exposed in an atmosphere with a low degree of pollution can be analyzed without preconcentration. However, the pH of the sample to be injected on the chromatographic column must be adjusted to between 6.0 and 12.0 in order to obtain reproducible sulfate values. For sulfation plates, the additivity of the deposition process is excellent for a period of exposure up to 3 months, with a reproducibility of about 2%. For nitration plates, the deposition process is not cumulative due to a physical change of the monitor during exposure. The correlation between the amounts of sulfate found on sulfation and nitration plates was also examined.

Keywords: Atmospheric corrosion, deposition measurement, sulfation plates, nitration plates, single-column ion chromatography

1. INTRODUCTION

Metallic objects exposed outdoors are subject to deterioration due to atmospheric pollution. In 1984, a joint US-Canadian atmospheric corrosion program was initiated to evaluate the impact of pollutants in the atmosphere on the corrosion of common metals. In Canada, the Experimental Lakes Area (Ontario) was selected as baseline site because it is known to be relatively unpolluted (Hechler, 1987a). At the same time, similar experiments were done on more polluted sites located in the United States (Flinn at al., 1985).

Traditionally, metallic panels were exposed on a particular site for different periods of time in order to measure the weight loss and then to calculate the rate of corrosion. Many environmental variables can influence atmospheric corrosion. The most significant are temperature, sunlight, wind, humidity and contaminants (Baker et al., 1982). Generally, mathematical models are developed to describe the weight losses as a function of the time of wetness and aggressivity of the atmosphere (Benarie et al., 1986).

In the present corrosion program, moisture sensors were used to measure the time of wetness in addition to the classical outdoor exposure of metals. The deposition of atmospheric contaminants was evaluated using passive monitors such as sulfation and nitration plates. Simplicity of use and low cost of operation represent the main advantages of these devices.

Atmospheric pollutants such as SO_X and NO_X are known to be corrosive. The damage occurs when corrosive species in the atmosphere are in contact with the metal surface. The deposition process of these corrosive substances is characterized by the concept of deposition velocity, which is related to the flux of pollutants per unit area and to the concentration of pollutants. A concentration measurement alone is not enough, and the concentration plus the wind velocity must be used to obtain a better approximation of the true deposition (Benarie et al.,1986; Haynie, 1980). The deposition velocity of these species on a given metal cannot be easily evaluated, and hence sulfation and nitration plates were used to estimate the deposition rate of SO_X and NO_X. These deposition velocity sensitive methods relate much better to corrosion damage than concentration measurements. Sulfation plates are made with a lead peroxide paste whereas nitration plates consist of an inert support impregnated with a triethanolamine solution (Huey, 1968; Levaggi et al., 1973; Levadie, 1979). These materials are put in small plastic Petrie dishes which are installed in an inverted position.

These passive monitors are generally used to determine the gas phase concentration of pollutants. This determination involves the estimation of a calibration factor which depends on several environmental variables. The sensitivity of the calibration factor to

variables such as the pollutant concentration and the wind speed was examined in a well-controlled atmosphere for sulfation and nitration plates (Sickles et al., 1987).

The objective of this work is to verify the performance of sulfation and nitration plates in a real environment with respect to their efficiency for evaluating the deposition of corrosive pollutants. A series of plates was exposed outdoors for periods of time varying from 2 weeks to 3 months. These different exposure times will show whether the additivity of pollutant concentrations is maintained over a period of 3 months. Also, it is known that SO_2 is absorbed on nitration plates, and thus the correlation between the sulfate concentration found on the two types of plates will be examined. Single-column ion chromatography (SCIC) was used to measure the amount of anions deposited on these passive monitors (Noël et al., 1988). Specific problems related to this technique were observed for the analysis of plates exposed to an atmosphere with a very low degree of pollution, and a brief discussion will be presented.

2. EXPERIMENTAL SECTION

2.1 Instrumentation and chemicals

The SCIC system consisted of a Series 3B liquid chromatograph from Perkin-Elmer (Norwalk, CT, U.S.A.) with a Model 7126 automatic universal injector (50 µL loop) from Rheodyne (Cotati, CA, U.S.A.). The detector was a Model 430 conductivity detector from Waters (Milford, MA, U.S.A.). Chromatograms were recorded on a Varian DS 604 data station (Walnut Creek, CA, U.S.A.). The ion-exchange column was an IC-PAK Anion column, 5 cm x 4.6 mm I.D., 10 µm particles, from Waters. The stationary phase is a polymethacrylate gel (spherical particles) with quaternary ammonium groups ($-C_2H_4N(CH_2CH_3)_3^+$) with an ion-exchange capacity of 0.06 meq/column (Glatz, 1985).

All chemicals were ACS certified reagent grade (Fisher Scientific Co., Fair Lawn, NJ, U.S.A.) unless otherwise stated. Deionized water was purified with the NanoPure II ion-exchange system from Sybron-Barnstead (Boston, MA, U.S.A.). Sulfation and nitration plates were obtained from Serco Laboratories (Cedar Falls, IA, U.S.A.) and have an adsorption surface of 18 cm^2.

2.2 Procedures

A phthalate eluent was used for the ion chromatography. A stock solution was made by dissolving 15.32 g of potassium hydrogen phthalate (KHP) in 1 liter of deionized water to give a 75 mM solution. A fresh solution of 0.75 mM KHP was prepared each day

and the pH of the eluent was adjusted to 6.5 with a 1 M solution of KOH. The KHP eluent was filtered and degassed in an ultrasonic bath for about 15 minutes.

For the analysis of the sulfation plates, the lead peroxide paste was carefully removed with a spatula and a stream of deionized water. A volume of 20 mL of Na_2CO_3 solution (0.47 M) was added to the mixture of water and PbO_2 paste. The solution was allowed to stand for 3 hours with occasional stirring and then it was placed in water at 100 °C for 30 minutes. After this it was topped up to a final volume of 50 mL and filtered through a Whatman No.42 paper filter. An aliquot of this solution was diluted five times in deionized water and adjusted to a pH of 6.5 with HCl. The final solution was filtered through a 0.45 µm Millex-HV filter before injection on the column.

For the analysis of nitration plates, the triethanolamine coating was removed with a spatula and a stream of deionized water, and the volume of the solution was brought to 50 mL. After 10 minutes, it was filtered through a Whatman No.1 paper filter. Finally, it was filtered through a 0.45 µm Millex-HV filter before injection on the column.

Passive monitors were exposed in an inverted position on a standard ASTM rack (ASTM G50-76) located at the NRC atmospheric test site in Boucherville, Québec. This site is in a semi-industrial location. Some environmental data concerning this site during the period of exposure are given in Table 1. The following mean annual pollutant concentrations have been determined: SO_2 = 20 µg/m^3; NO_2 = 40 µg/m^3; NO_3 = 35 µg/m^3. For each period of exposure, two plates of both types were analyzed.

3. RESULTS AND DISCUSSION

3.1 Single-column ion chromatography

Turbidimetry and colorimetry are the analytical procedures proposed by the manufacturer of sulfation and nitration plates to determine respectively the level of sulfate and nitrite anions absorbed by the monitors. These analytical methods are classic and well documented in the literature (Huey, 1968; Levaggi et al., 1973). Turbidimetry involves the precipitation of barium sulfate after conversion of the insoluble lead sulfate to a soluble lead carbonate (Huey, 1968). Nitrite determination is done with a colorimetric method involving the complexation of N-1-naphthylethylenediamine dihydrochloride (NEDA) with the reaction product of sulfanilamide and nitrite. This method is sensitive and precise but works only for the nitrite anion (Levaggi et al., 1973). However, nitrate and sulfate anions are also absorbed on the nitration plate (Sickles et al., 1987). Thus, the colorimetric

method gives only partial information and other analytical procedures must be used to obtain a complete analysis of nitration plates.

The estimation of atmospheric corrosion data for a baseline site requires the determination of very low levels of SO_X and NO_X deposition on passive monitors. Previous work has shown that turbidimetry is unsuitable for the quantitative analysis of sulfation plates if concentrations of SO_2 in the atmosphere are low (Noël et al., 1988). Turbidimetry cannot detect absorbed sulfate quantities lower than 2.5 mg/plate because the calibration curve is not linear at low sulfate concentration, and also because absorbances at these levels of sulfate are very low. In addition, many experimental factors can influence the turbidity of the solution and reproducible results are extremely difficult to obtain. Preliminary results indicate that the quantity of sulfate absorbed on a sulfation plate exposed in an atmosphere with a very low degree of pollution can be as low as 200 µg/plate after an exposure time of 3 months. By comparison, a sulfation plate exposed in an urban area generally absorbs more than 3.0 mg/plate of sulfate. In the latter case, turbidimetry can be used if correct analytical procedures are respected.

During the past few years, ion chromatography has become a powerful technique for analyzing various types of passive monitors (Crowther et al., 1981; Tarter, 1987). Basically, there are two variants of ion chromatography, namely single-column ion chromatography (SCIC) and eluent-suppressed ion chromatography (ESIC). In SCIC, the suppressor column, which is installed after the separation column in ESIC, is eliminated because the ion separation is achieved using a low conductivity eluent. Thus, a conventional liquid chromatograph can be used with SCIC. This technique was used with success to analyze contaminants in atmospheric aerosols (Baltensperger et al., 1985; Willison et al., 1984) and it was used in this work to analyze sulfation and nitration plates.

As described in the Experimental section, the chemical treatment of sulfation plates to obtain soluble sulfate gives a highly basic solution (pH 12-13) with a relatively complex matrix due to the addition of sodium carbonate. Different chromatographic conditions were tried in order to analyze this solution, and a 0.75 mM phthalate eluent (KHP) adjusted to pH 6.5 gives the best results with an IC-PAK Anion column (Noël et al., 1988). The final solution obtained after the treatment of a nitration plate is less complex than for a sulfation plate but the same eluent was used for the analysis of the two types of passive monitors since the separation of nitrite, nitrate and sulfate was excellent using these chromatographic conditions.

Fig. 1 shows typical chromatograms obtained on injecting solutions made from sulfation and nitration plates. For the sulfation plate (Fig.1A), the solution is diluted five times with water to reduce the amount of carbonate, which hides the sulfate peak, and it is

neutralized with HCl to bring its pH to a value similar to the pH of the eluent. Injection of a non-neutralized sample causes the coelution of a system peak with the sulfate peak, preventing an accurate determination of the peak area whereas the injection of a neutralized solution eliminates the system peak. For the nitration plate (Fig.1B), there is no addition of sodium carbonate to the solution. Thus, no particular treatment before injection on the chromatographic column is necessary and the separation of nitrite, nitrate and sulfate anions is easily achieved with the KHP eluent. Using conductivity detection, the limit of detection for the sulfate anion is about 300 ppb for an injection of 50 µL, or 15 ng of sulfate. Indirect UV detection can also be used to decrease the limit of detection to about 100 ppb of sulfate. Consequently, SCIC allows the quantitation of passive monitors exposed to an atmosphere with low pollution and it should be preferred to conventional analytical methods such as turbidimetry or colorimetry.

Fig. 2 emphasizes the importance of an adequate chemical treatment of the solution before the injection on the column in order to analyze the sulfate anion. It shows the variation of the sulfate peak area as a function of the pH of the sample. This curve was obtained by injecting standard solutions of 10 ppm of sulfate adjusted to the appropriate pH. A significant increase of the peak area is observed for pH lower than 6.0 whereas the peak area remains constant for pH higher than 6.0. A more systematic study of this behavior has shown that this variation can be related to the degree of dissociation of the eluent (Noël et al., 1988). Consequently, it is very important to control the pH of the sample for a quantitative analysis of sulfate. This control must be applied not only to passive monitors but also to any other types of environmental samples with pH lower than 6.0 if sulfate determination is required.

3.2 Sulfation plates

Sulfation and nitration plates are extremely sensitive to wind velocity, and the monitoring of the air quality with these devices is subject to uncertainties (Sickles et al., 1987). However, the deposition of atmospheric contaminants on metallic surfaces can be estimated using these plates. For a given period of outdoors exposure, it was observed that there is a good correlation between the amount of sulfur deposited on metal and the quantity of sulfate absorbed on sulfation plates (Hechler et al., 1987b). Their performance in a real environment must be evaluated in order to verify if the additivity of the deposition process of contaminants is respected for a given period of time and also to estimate their life time for an outdoor exposure.

All the exposed plates were taken from the same lot to avoid lot-to-lot differences. Table 2 reports the results obtained for each plate. The quantity of sulfate corresponds to the average of three determinations and the relative standard deviation is generally lower than 5%. The values in Table 2 were corrected for the blank obtained with a non-exposed plate. For this lot, the quantity of sulfate for the blank (431 μg/plate) is significantly higher than for the blanks analyzed by Sickles and Michie (1987). They found that the level of sulfate in a non-exposed plate varied between 19 and 268 μg/plate. Thus, the lot-to-lot differences for sulfation plates are significant and corrections must be done for each lot.

Generally, quantities of sulfate found on two different plates exposed for the same period of time are similar and indicate a good reproducibility of the absorption of SO_2 on the PbO_2 paste. The levels of sulfate for the three periods of 4 weeks and for the 2 periods of 6 weeks are not similar when compared between them because the plates were exposed consecutively and climatic conditions changed during the exposure time. The diagram illustrating the periods of exposure is given in Fig. 3. For each period of exposure, it shows when sulfation plates were exposed and the level of sulfate found by ion chromatography. The plates were exposed during the 1986 fall season from the beginning of September to the end of November.

Fig. 3 shows that for a given period of exposure, for example 4 or 6 weeks, the quantity of sulfate collected by the plates increases with time. Fig. 4 illustrates graphically the variation of the level of sulfate as a function of the exposure time for the periods beginning in September. The relation is not linear because the uptake of SO_2 has increased during this time. Thus, the response of the plates to atmospheric variations seems adequate and it is highly probable that a metallic surface exposed in the same conditions would also have been in contact with an increasing quantity of SO_2. The levels of sulfate in the column labeled "Total" represent the sum of different periods of exposure giving a total period of 12 weeks. It is remarkable that for a period of 3 months, these values are identical, with an average of 3120 ± 72 μg/plate and a relative standard deviation of 2.3%. The error of measurement is larger for a short period of exposure such as 2 weeks since the sulfate value is similar to the value of the blank. Thus, it is highly probable that the sum of the periods of 10 + 2 weeks gives a value with a larger error. In fact, this value is slightly lower than the others. If this value of 3011 μg/plate is not used, the average of the total values is 3148 ± 45 μg/plate with a relative standard deviation of 1.4%. The addition of two periods of 4 weeks gives also a concentration of sulfate (1858 μg/plate) identical to the value found for the period of 8 weeks (1876 μg/plate). These results indicate the excellent additivity of sulfation plates in a real environment. These plates can be exposed without problems for periods of time up to at least 3 months. However, it is important to analyze

the plates as soon as possible after their exposure. Table 2 shows that the sulfate value found on a plate stored in a glovebox under inert atmosphere for a period of 1.5 years gives lower values. This decrease in the level of sulfate is probably related to difficulty in extracting the sulfate efficiently due to a physical change in the PbO_2 paste.

3.3 Nitration plates

Nitration plates were exposed with sulfation plates during the same period. Table 3 summarizes the results obtained for the determination of nitrite, nitrate and sulfate anions. As for sulfation plates, the values reported in Table 3 are corrected for the blanks. The values for the blank are similar to those reported by Sickles and Michie (Sickles et al., 1987). They found for nitrite, nitrate, and sulfate, values varying respectively between 18-39, 9-196 and 5-294 µg/plate.

In contrast to sulfation plates, variations between two nitration plates are large, and thus errors of measurement with these devices are important. After an exposure of two weeks, the levels of contaminants are almost negligible. As illustrated in Fig. 5, there is almost no absorption of nitrite and nitrate before 5 or 6 weeks. After this time, a gradual increase of the quantity of nitrite and nitrate absorbed on the plates is observed. The only exception is the nitrite value for the plates exposed during twelve weeks. In this case, both plates give a low nitrite value indicating that this phenomenon is not an artifact. However, there is currently no explanation for this behavior.

The additivity for the nitration plates with respect to the quantity of nitrite, nitrate and sulfate anions is given in Table 4. Clearly, the absorption of anions on nitration plates is not cumulative. This behavior is particularly true for the nitrite anion. For nitrate and sulfate anions, the sums found for 8+4 weeks and 6+6 weeks are relatively similar. However, these values are not as high as for the plates exposed for the total period of 12 weeks. In all cases, the levels of anions for an exposure of 4 weeks are unusually low and this indicates a variation in the mechanism of adsorption after this period.

Physically, the appearance of the nitration plates changes during the exposure. In its initial condition, the material in the plate is wet and the texture is slightly gelatinous. After two or three weeks, the material becomes dry. It is unlikely that triethanolamine (TEA) is removed by evaporation because TEA has a high viscosity and low vapor pressure. In addition, infrared spectroscopy has confirmed that TEA is present on the plate even after an exposure of 12 weeks. The composition of the TEA coating is unknown and it is difficult to identify the exact cause of the drying of the nitration plate. However, this change in the physical condition of nitration plates may explain the poor results obtained in

Table 4. During the first period of exposure, there is probably a continuous exchange between the plate and the atmosphere with a release of absorbed anions due to the metamorphosis of the coating. This exchange explains the low levels of anions measured before 6 weeks (Table 4 and Fig. 5). After a certain period of time (3-4 weeks), the plates achieve a relatively stable state, and the anions are captured by the monitors probably via an adsorption mechanism. This can explain why the results obtained for intermediate exposure times are more similar (8+4 and 6+6 weeks). However, the adsorption behavior is probably not reproducible and this is why the results obtained after a total exposure of 12 weeks are not in good agreement with other results.

In conclusion, nitration plates cannot be used in a real environment to evaluate the deposition concentration of anions.

3.4 Comparison of sulfation and nitration plates for the determination of sulfate

Fig. 6 shows the variation of the sulfate level measured on nitration plates as a function of the exposure time. The trend is very similar to the one observed in Fig. 4 with sulfation plates. For a short period of time, exposure of nitration and sulfation plates to SO_2 gives comparable SO_2 deposition values in well-controlled conditions (Sickles et al., 1987). Table 5 summarizes the level of sulfate found on the two types of device, together with the ratio of the two determinations. Clearly, the value of sulfate found on sulfation plates is superior to the quantity found on nitration plates. Also, as the exposure time increases, the ratio of the two determinations decreases, indicating that nitration plates cannot be used for the determination of sulfate.

4. CONCLUSION

Analysis of passive monitors exposed in an atmosphere with a low degree of pollution requires an ion chromatographic technique to quantitate low amounts of pollutants. Single-column ion chromatography with a phthalate eluent appears to be a suitable solution for rapid analysis of both sulfation and nitration plates. However, it is very important to control the pH of the sample for the analysis of sulfate. It was shown that the sulfate peak area remains constant for a sample pH varying between 6.0 and 12.0. At lower pH, there is a significant increase of the area and the reproducibility of the determination is decreased.

Sulfation plates are suitable for evaluating the deposition of SO_2 in a real environment. They can be used up to at least 3 months without problems and the additivity

of the deposition process is excellent. For a period of exposure of 3 months, the sums of the sulfate values found for shorter periods of time are reproducible to about 2%. However, it is important to analyze the plates as soon as possible after their exposure. The additivity of pollutants on nitration plates is not good for an outdoors exposure. After an exposure of 3 or 4 weeks, the physical aspect of the nitration plate changes and the absorption of pollutants is not cumulative. In addition to the absorption of nitrite, there is also the absorption of nitrate and sulfate on nitration plates. Unfortunately, for a relatively long outdoors exposure, there is no correlation between the sulfate values found on the two types of plate. In conclusion, sulfate plates are excellent for estimating atmospheric deposition, whereas nitration plates are unsuitable and should not be used for atmospheric corrosion studies.

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Table 1: Environmental data on the NRC test site (Boucherville, Québec) for the period of exposure.

Parameter		September	October	November
Relative humidity	daily mean maximum	93	90	89
	daily mean minimum	60	56	56
Wind	Prevailing direction	South	North	South
	mean speed (km/h)	14.2	12.9	14.2
Temperature (°C)	daily mean maximum	18.0	12.6	4.0
	Daily mean minimum	7.7	2.3	-4.7

Table 2: Levels of sulfate anion determined on sulfation plates for various exposure times.

Exposure (weeks)	Sulfate (µg/plate)		Average (µg/plate)
2[a]	319	331	325
2[b]	450	520	485
2[c]	285	280	283
4	707	657	682
4	1144	1207	1176
4	1381	1257	1319
6	1281	1419	1350
6	1731	1794	1762
8	1794	1957	1876
10	2357	2694	2526
12	3019	3194	3107
blank	425	458	431

[a] Exposed at the beginning of September

[b] Exposed at the end of the period of 10 weeks

[c] Exposed at the beginning of September but analyzed 1.5 years later

Table 3: Concentrations of nitrite, nitrate and sulfate anions determined on nitration plates for various exposure times.

Exposure (weeks)	Nitrite (µg/plate)		Average (µg/plate)	Nitrate (µg/plate)		Average (µg/plate)	Sulfate (µg/plate)		Average (µg/plate)
2[a]	0	0	0	17	39	28	20	42	31
4	0	0	0	37	15	26	295	190	242
4	0	6	3	24	30	27	290	285	287
4	0	0	0	47	85	66	310	270	290
6	58	48	53	119	60	90	590	445	518
6	154	0	77	142	132	137	658	642	650
8	63	103	83	127	159	143	1000	872	936
10	140	166	153	292	272	282	1158	1192	1175
12	66	68	67	289	312	301	1580	1800	1690
blank	48	55	52	128	178	153	275	325	300

[a] Exposed at the beginning of September

Table 4: Additivity of the anions absorbed on nitration plates.

	Duration of exposure					
	12 weeks				8 weeks	
Sum -->	12	8+4	4+4+4	6+6	8	4+4
nitrite	67	83	3	130	83	3
nitrate	301	209	119	227	143	53
sulfate	1690	1226	817	1168	936	517

Table 5: Comparison of the level of sulfate found on sulfation and nitration plates.

Exposure (weeks)	Sulfation (µg/plate)	Nitration (µg/plate)	Ratio
2	325	31	10.5
4	682	242	2.82
4	1176	285	4.13
4	1319	290	4.54
6	1350	518	2.61
6	1762	650	2.71
8	1876	936	2.00
10	2526	1175	2.15
12	3107	1690	1.84

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Figure 2: Effect of the sample pH on the sulfate peak area. See Experimental Section for details.

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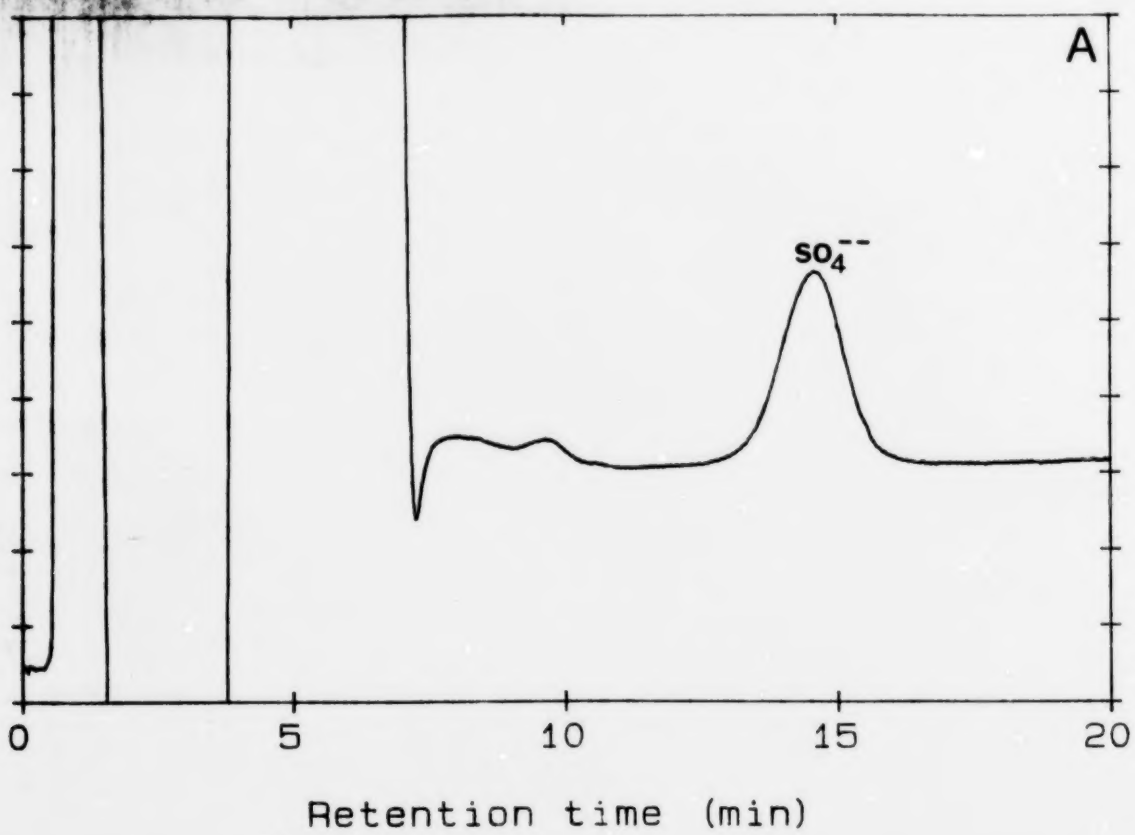
Figure 4: Variation of the level of sulfate absorbed on sulfation plates as a function of the exposure time.

Figure 5: Variation of the level of nitrite (■) and nitrate (□) anions absorbed on nitration plates as a function of the exposure time.

Figure 6: Variation of the level of sulfate anions absorbed on nitration plates as a function of the exposure time.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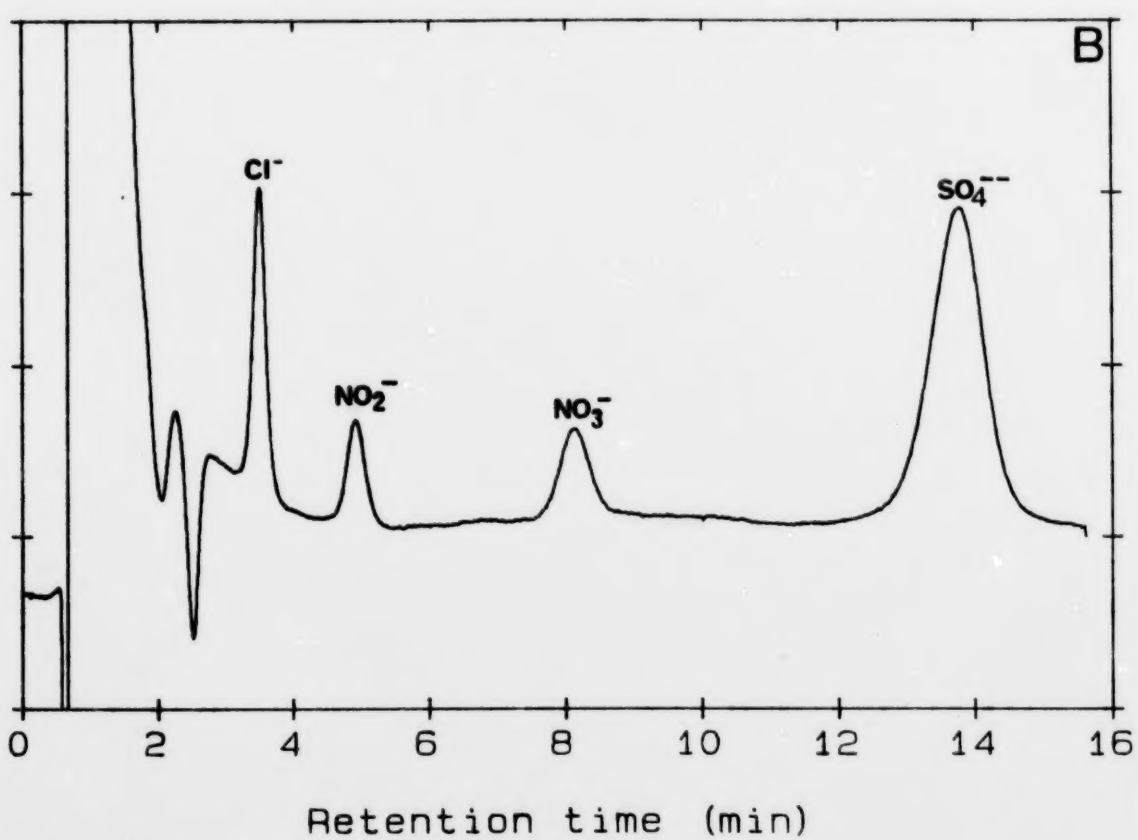
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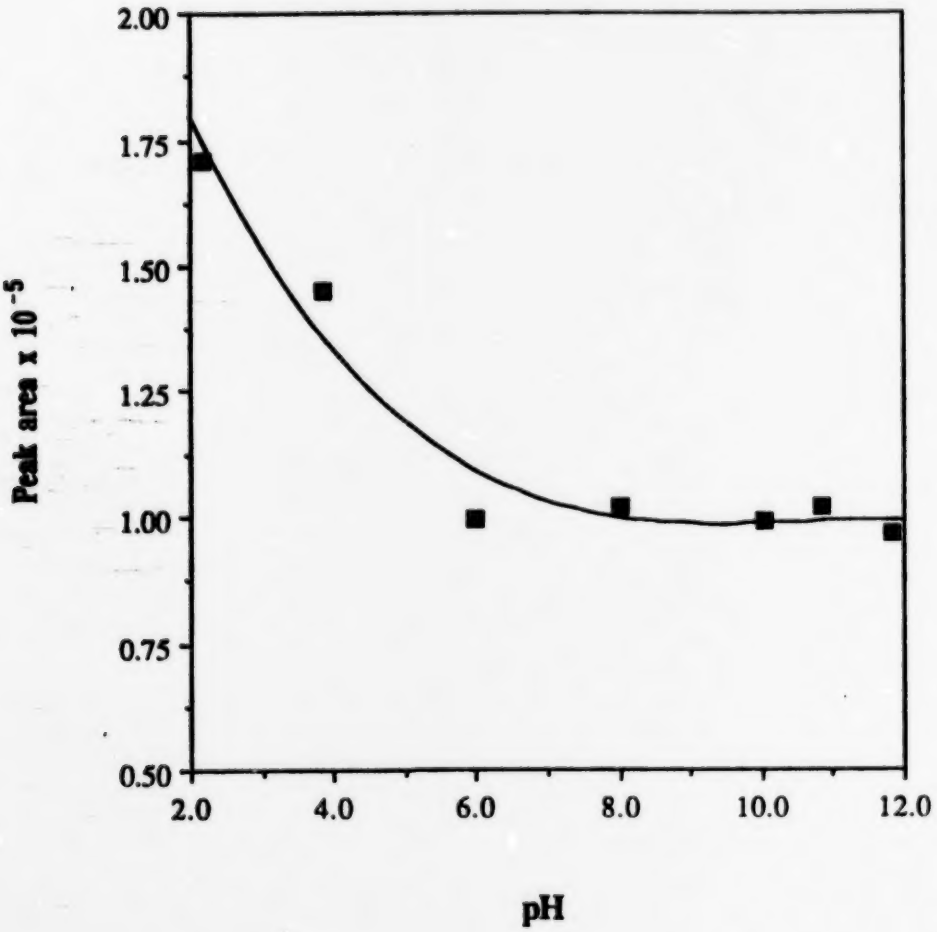
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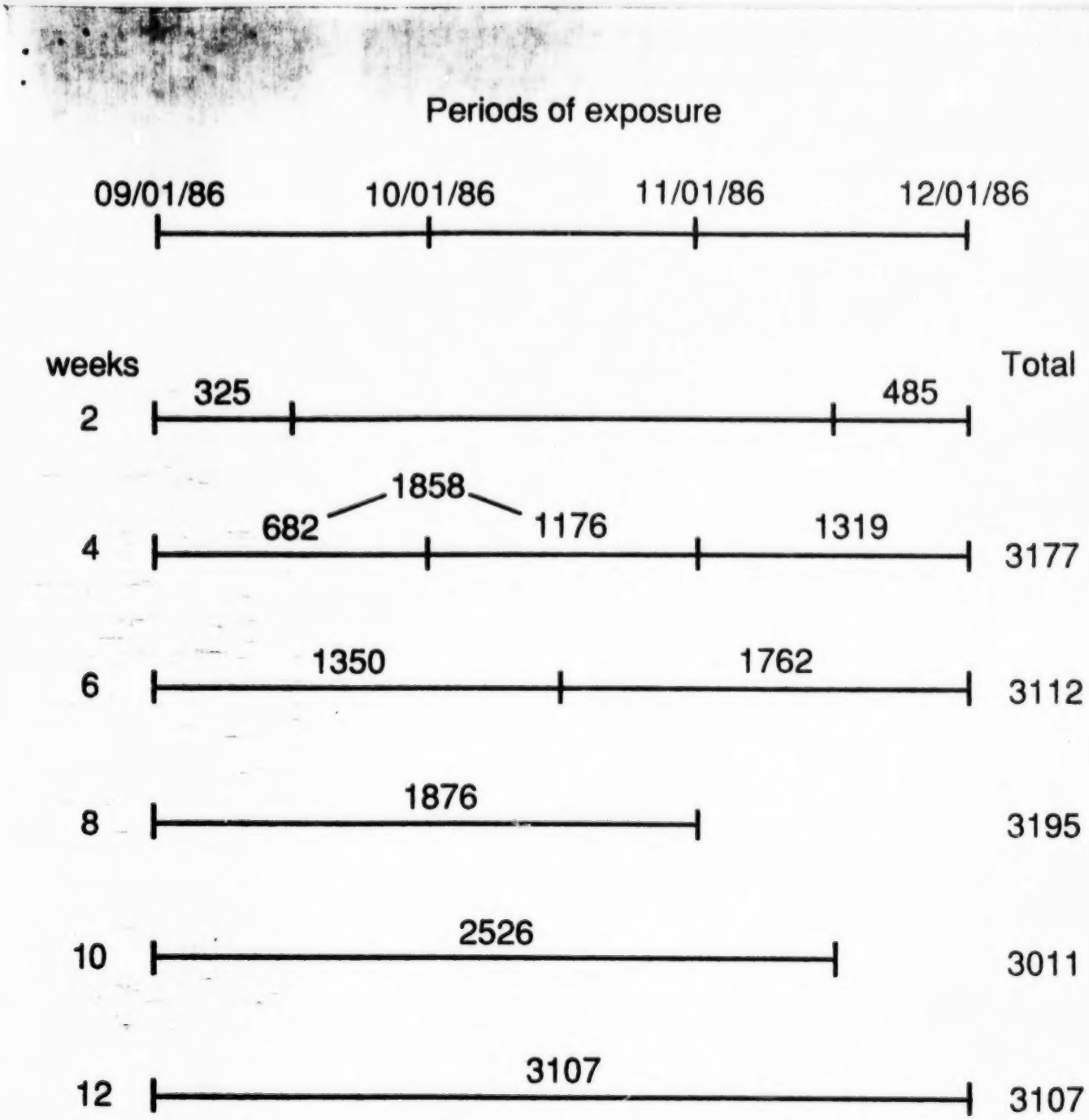
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09/01/86
10/01/86
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12/01/86
weeks
Total
2
325
485
4
1858
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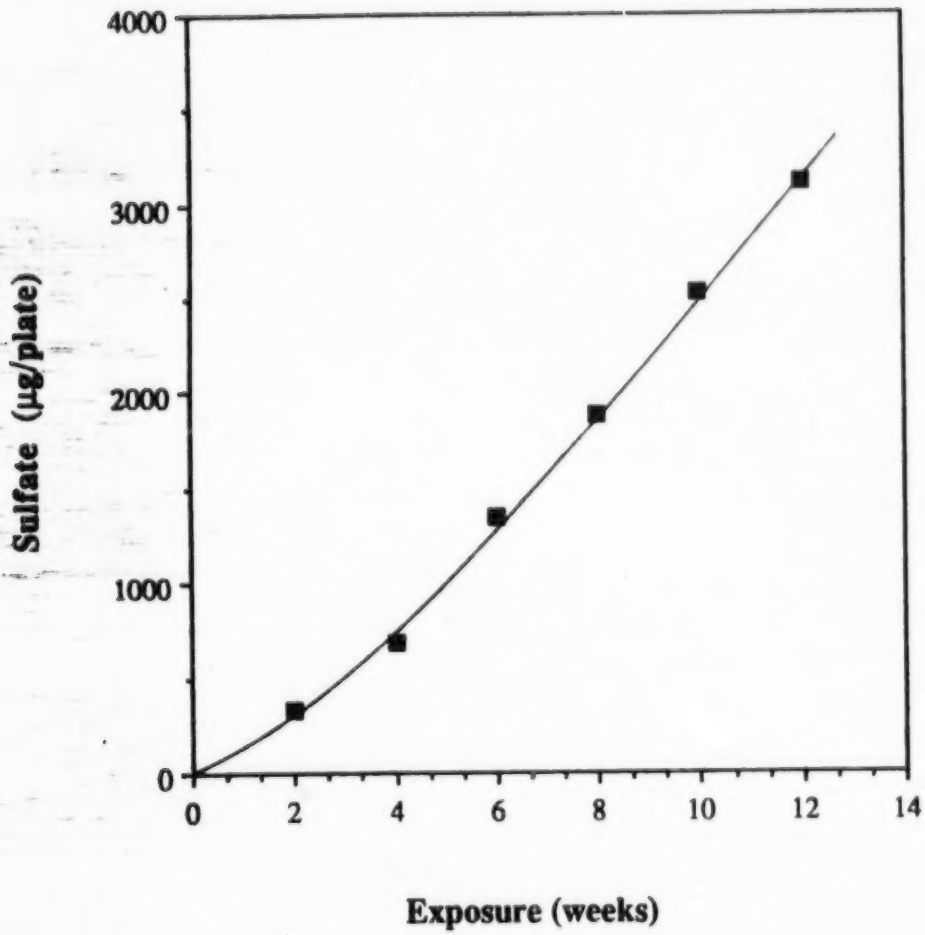
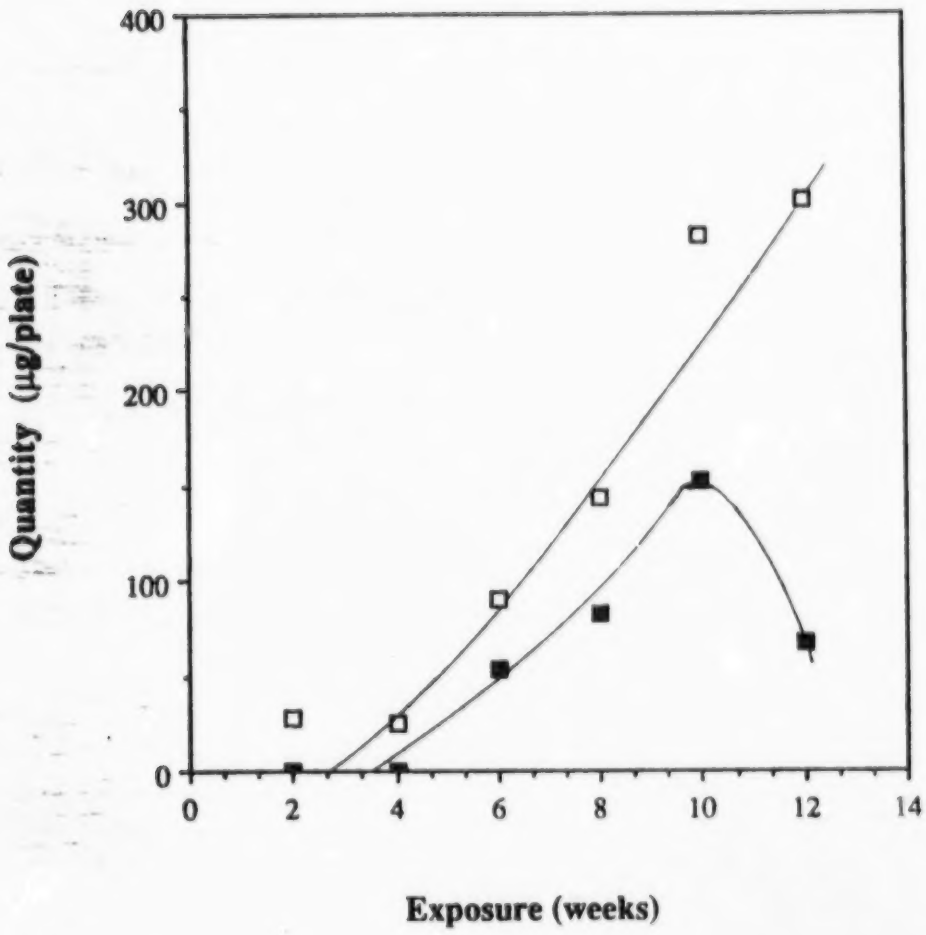
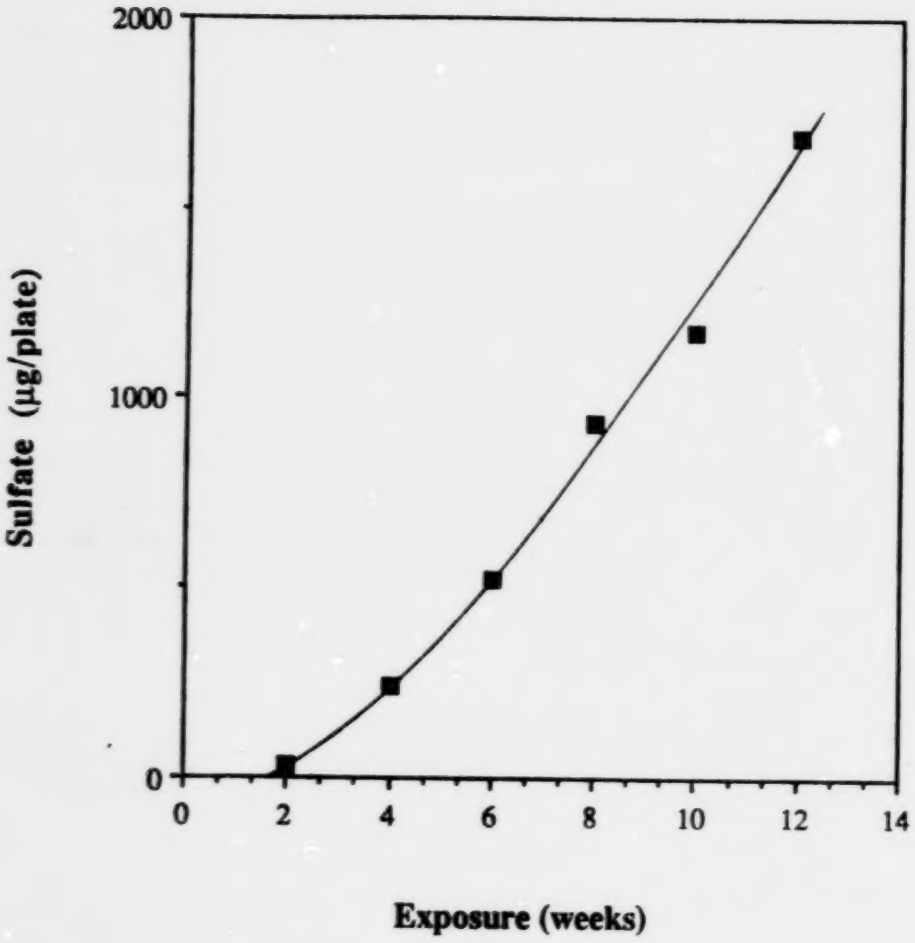
1176
1319
3177
6
1350
1762
3112
8
1876
3195
10
2526
3011
12
3107
3107


4000
3000
2000
1000
0
Sulfate (µg/plate)
0
2
4
6
8
10
12
14
Exposure (weeks)


400
300
200
100
0
Quantity (µg/plate)
0
2
4
6
8
10
12
14
Exposure (weeks)


2000
1000
0
Sulfate (µg/plate)
0
2
4
6
8
10
12
14
Exposure (weeks)